

## Claims

1. A process for producing proton-conducting polymer membranes, which comprises the steps
  - A) preparation of a mixture comprising polyphosphoric acid, at least one polyazole and/or one or more compounds suitable for forming polyazoles under the action of heat in step B),
  - B) heating of the mixture obtainable according to step A) to temperatures up to 400°C under inert gas,
  - C) application of a layer to a support using the mixture from step A) and/or B),
  - D) treatment of the membrane formed in step C), characterized in that the treatment of the membrane is carried out using a hydrolysis liquid comprising oxo acids of phosphorus and/or oxo acids of sulfur.
2. The process as claimed in claim 1, characterized in that the mixture prepared in step A) comprises compounds suitable for forming polyazoles under the action of heat in step B), with these compounds comprising one or more aromatic and/or heteroaromatic tetraamino compounds and one or more aromatic and/or heteroaromatic carboxylic acids or derivatives thereof which contain at least two acid groups per carboxylic acid monomer, and/or one or more aromatic and/or heteroaromatic diaminocarboxylic acids.
3. The process as claimed in claim 1, characterized in that the mixture prepared in step A) comprises compounds suitable for forming polyazoles under the action of heat in step B), with these compounds being obtainable by reaction of one or more aromatic and/or heteroaromatic tetraamino compounds with one or more aromatic and/or heteroaromatic carboxylic acids or derivatives thereof which contain at least two acid groups per carboxylic acid monomer or of one or more aromatic and/or heteroaromatic diamino carboxylic acids in the melt at temperatures of up to 400°C.
4. The process as claimed in claim 2 or 3, characterized in that the compounds suitable for forming polyazoles comprise, as aromatic and/or heteroaromatic tetraamino compounds, compounds selected from the group consisting of 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine and/or 1,2,4,5-tetraaminobenzene.

5. The process as claimed in claim 2, 3 or 4, characterized in that the compounds suitable for forming polyazoles comprise, as aromatic and/or heteroaromatic carboxylic acids or derivatives thereof which contain at least two acid groups per carboxylic acid monomer, compounds selected from the group consisting of isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dihydroxyisophthalic acid, 2,3-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, bis(4-carboxyphenyl) ether, benzophenone-4,4'-dicarboxylic acid, bis(4-carboxyphenyl) sulfone, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid, or C1-C20-alkyl esters or C5-C12-aryl esters thereof, or anhydrides thereof or acid chlorides thereof.
6. The process as claimed in claim 2, 3, 4 or 5, characterized in that the compounds suitable for forming polyazoles comprise aromatic tricarboxylic acids, C1-C20-alkyl esters or C5-C12-aryl esters thereof or anhydrides thereof or acid halides thereof or tetracarboxylic acids, C1-C20-alkyl esters or C5-C12-aryl esters thereof or anhydrides thereof or acid halides thereof.
7. The process as claimed in claim 6, characterized in that the aromatic tricarboxylic acids comprise compounds selected from the group consisting of 1,3,5-benzenetricarboxylic acid (trimesic acid); 2,4,5-benzenetricarboxylic acid (trimellitic acid); (2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphenyltricarboxylic acid; 3,5,4'-biphenyltricarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acid; naphthalene-1,4,5,8-tetracarboxylic acid, 3,5,3',5'-biphenyltetracarboxylic acid, benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid and/or 1,4,5,8-naphthalenetetracarboxylic acid.
8. The process as claimed in claim 6 or 7, characterized in that the content of tricarboxylic acids and/or tetracarboxylic acids is in the range from 0 to

30 mol%, preferably from 0.1 to 20 mol%, in particular from 0.5 to 10 mol%, based on dicarboxylic acid used.

- 5 9. The process as claimed in one or more of claims 2 to 8, wherein the compounds suitable for forming polyazoles comprise heteroaromatic dicarboxylic acids, tricarboxylic acids and/or tetracarboxylic acids containing at least one nitrogen, oxygen, sulfur or phosphorus atom in the aromatic.
- 10 10. The process as claimed in claim 9, characterized in that pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid, and also C1-C20-alkyl esters or C5-C12-aryl esters thereof, or anhydrides thereof or acid chlorides thereof are used.
- 15 11. The process as claimed in claim 2 or 3, characterized in that the compounds suitable for forming polyazoles comprise diaminobenzoic acid and/or monohydrochloride and dihydrochloride derivatives thereof.
- 20 12. The process as claimed in any of the preceding claims, characterized in that at least one further polymer (polymer B) which is not a polyazole is added to the composition obtainable in step A) and/or step B), with the weight ratio of polyazole to polymer B being in the range from 0.1 to 50.
- 25 13. The process as claimed in any of the preceding claims, characterized in that the heating according to step B) is carried out after formation of a sheet-like structure in step C).
- 30 14. The process as claimed in any of the preceding claims, characterized in that the treatment according to step D) is carried out at temperatures in the range from 0°C to 150°C.
- 35 15. The process as claimed in any of the preceding claims, characterized in that the hydrolysis liquid comprises water in a concentration of from 5 to 80% by weight.
16. The process as claimed in any of the preceding claims, characterized in that phosphoric acid containing from 10 to 60% by weight of water is used as hydrolysis liquid.

17. The process as claimed in any of the preceding claims, characterized in that the hydrolysis liquid comprises phosphinic acid, phosphonic acid, phosphoric acid, hypodiphosphonic acid, hypodiphosphoric acid, oligophosphoric acids, sulfurous acid, disulfurous acid and/or sulfuric acid.
18. The process as claimed in any of the preceding claims, characterized in that the hydrolysis liquid comprises monomers which contain phosphonic acid and/or sulfonic acid groups and are capable of free-radical polymerization.
19. The process as claimed in any of the preceding claims, characterized in that the hydrolysis liquid comprises crosslinking monomers capable of free-radical polymerization.
20. The process as claimed in any of the preceding claims, characterized in that crosslinking monomers capable of free-radical polymerization are applied to the membrane after the hydrolysis.
21. The process as claimed in any of claims 18 to 20, characterized in that the monomers capable of free-radical polymerization are polymerized after the hydrolysis.
22. A proton-conducting polymer membrane obtainable by a process as claimed in any of claims 1 to 21, characterized in that the membrane has a phosphoric acid concentration of at least 85% by weight at a fracture toughness of at least 30 kJ/m<sup>2</sup>.
23. The proton-conducting polymer membrane obtainable by a process as claimed in any of claims 1 to 21, characterized in that the membrane has a phosphoric acid concentration of at least 95% by weight at a breaking stress of at least 10 kJ/m<sup>2</sup>.
24. The proton-conducting polymer membrane comprising phosphoric acid, at least one polyazole and at least one monomer which contains phosphonic acid and/or sulfonic acid groups and is capable of free-radical polymerization, characterized in that the ratio of the total weight of phosphoric acid, polyphosphoric acid and the hydrolysis products of polyphosphoric acid to the weight of the monomers capable of free-radical polymerization is greater than or equal to 1:2.

- 5 25. The proton-conducting polymer membrane as claimed in claim 20, characterized in that the ratio of the total weight of phosphoric acid, polyphosphoric acid and the hydrolysis products of polyphosphoric acid to the weight of the monomers capable of free-radical polymerization is from 100:1 to 5:1.
- 10 26. The proton-conducting polymer membrane as claimed in claim 24 or 25 which is obtainable by polymerizing the monomers capable of free-radical polymerization.
27. A membrane-electrode unit comprising at least one polymer membrane as claimed in any of claims 24 to 26.
- 15 28. A fuel cell comprising one or more membrane-electrode units as claimed in claim 27.